Microplastics: emerging trends and research gaps

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What are microplastics?

- Microplastics (MPs) are small plastic particles (e.g., fibers, fragments, films, and pellets) < 5 mm across (largest crosswise dimension) and > 100 nm.
- Two categories:
  - *Primary*: Designed to be small. (e.g., PE/PP microbeads in personal care products, glitter, industrial pellets ‘nurdles’)
  - *Secondary*: Breakdown of larger plastic debris, tire wear, nylon/polyester fibers shed from laundry.
- Particles < 100 nm have been classified as ‘nanoplastics’ (NPs). However, most relevant size fraction is still under discussion.

Where are microplastics?

- Microplastics are ubiquitous
  - Air
  - Soil
  - Water
  - Food & drink

FOOD FOR THOUGHT

Beer, Drinking Water And Fish: Tiny Plastic Is Everywhere

August 20, 2018 · 11:57 AM ET

ENVIRONMENT | PLANET OR PLASTIC?

Microplastics are raining down from the sky

Scientists discover large amounts of tiny plastic particles falling out of the air in a remote mountain location.

ENVIRONMENT 08/18/2019 10:26 am ET

Scientists Astonished After Finding Microplastics In Arctic Snow

Sources: huffpost.com, npr.org, nationalgeographic.com

Ecotoxicity and human health impacts

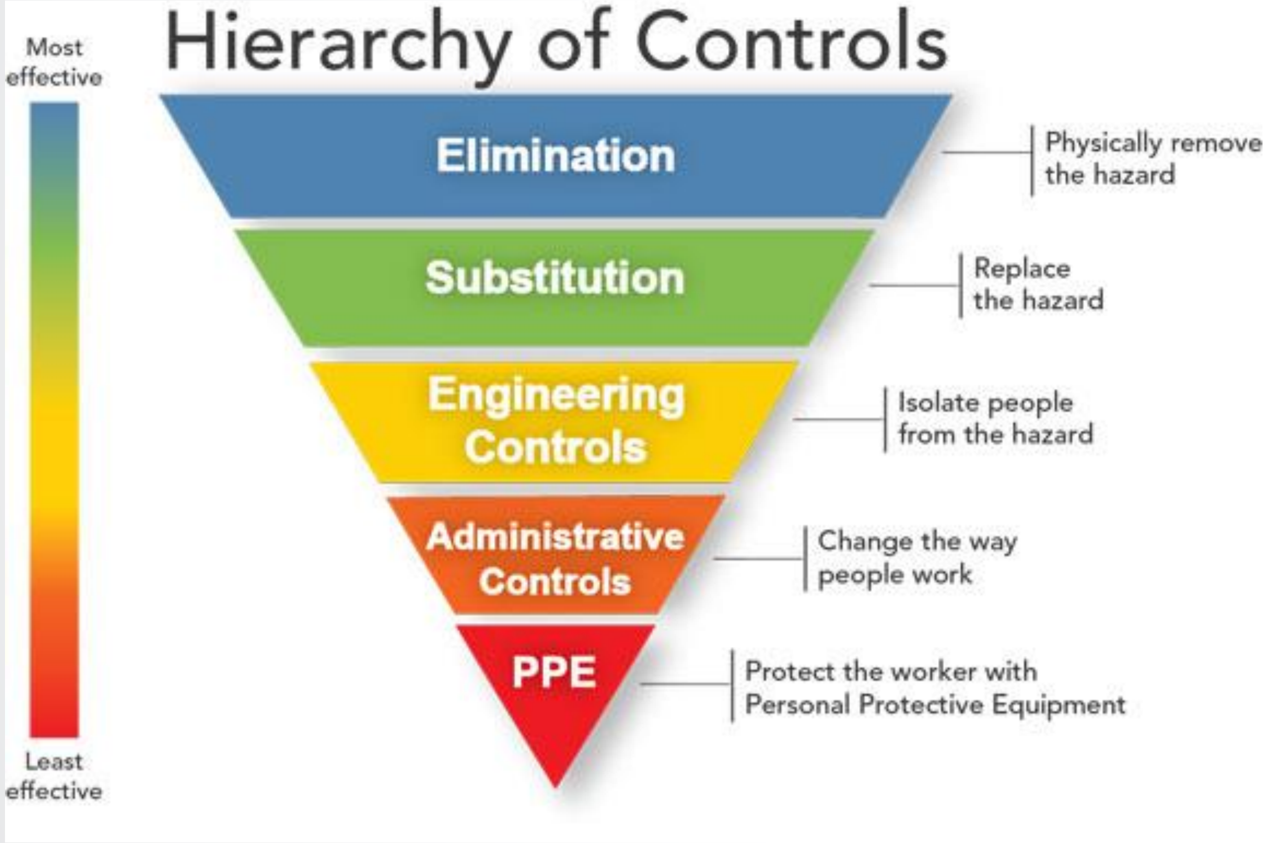
- Bioaccumulation affecting plants and small animals
- Respiratory effects
- Vectors for persistent organic pollutants (POPs) and plastic-associated chemicals (PACs)

Current analytical methods

- Separation from sample matrix
  - sieving, density separation, digestion of organic material
- Identification/characterization
  - Most common: μ-FTIR, μ-Raman
  - Less common: TGA-GC/MS, hyperspectral imaging

Most of these techniques can only be used on microplastics > 10 microns, need new methods for nanoplastics

Plastic waste – hazard control



- Elimination – stop using plastic
  - Not feasible in short term
- Substitution – use different polymers
  - Need to identify primary polymer targets for substitution

1. Geographical source – where are most MPs originating?
2. Polymer source – which polymer types are contributing the most MPs?

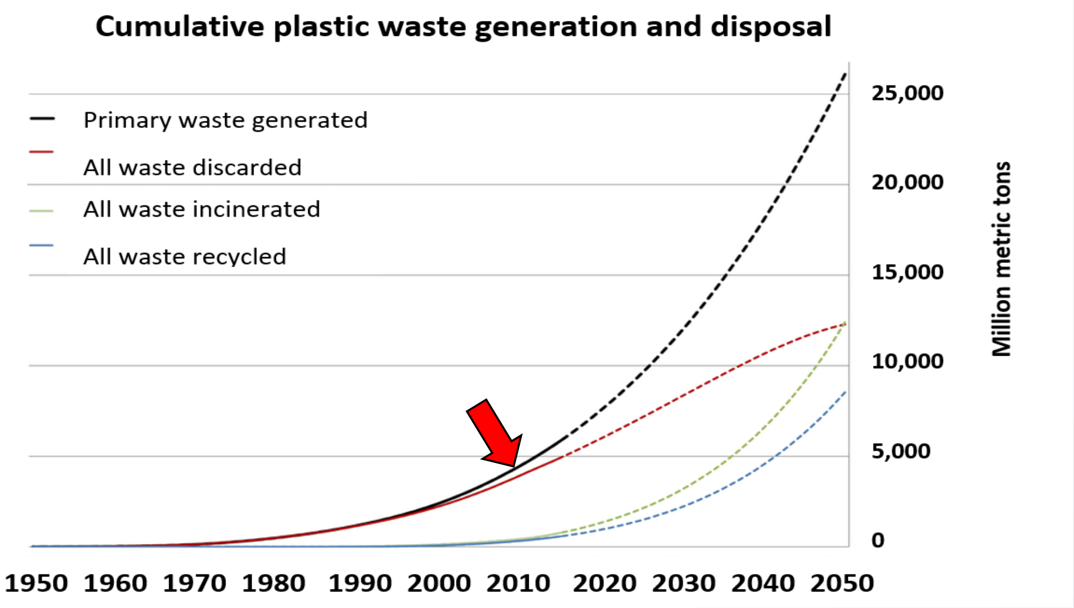
Source: https://www.cdc.gov/niosh/topics/hierarchy/default.html

MP monitoring: study limitations

- Manual µ-FTIR and µ-Raman methods are time-intensive, and biased due to particle selection and transfer for analysis. Automated methods needed.
- Weathering/transformations (UV degradation, biofilms) can alter spectra.
- Particles size limitations (ATR-FTIR > 500 µm, µ-FTIR down to 20 µm, Raman: low to sub-µm)
- Water collection methods can miss small MPs (and NPs) due to mesh opening (e.g., 300 µm). Filters limited to smaller volumes due to clogging.
- Direct comparisons of different studies generally not possible due to the many different methods used.

Why study MPs?

- Plastic is persistent, growing, and pervasive:
  - 8,300 Mt produced since 1950
  - 6,300 Mt waste generated: 79% in landfills or environment
  - 12,000 Mt discarded by 2050
- MPs are everywhere: Arctic, Antarctic, deep sea, ice cores, remote islands.
- Small particles can impact marine ecosystems globally
- Freshwaters are sources, especially in urban areas, but not well studied.
- Environmental and health impacts uncertain



Source: Cumulative plastic waste generation and disposal, Geyer (2017)

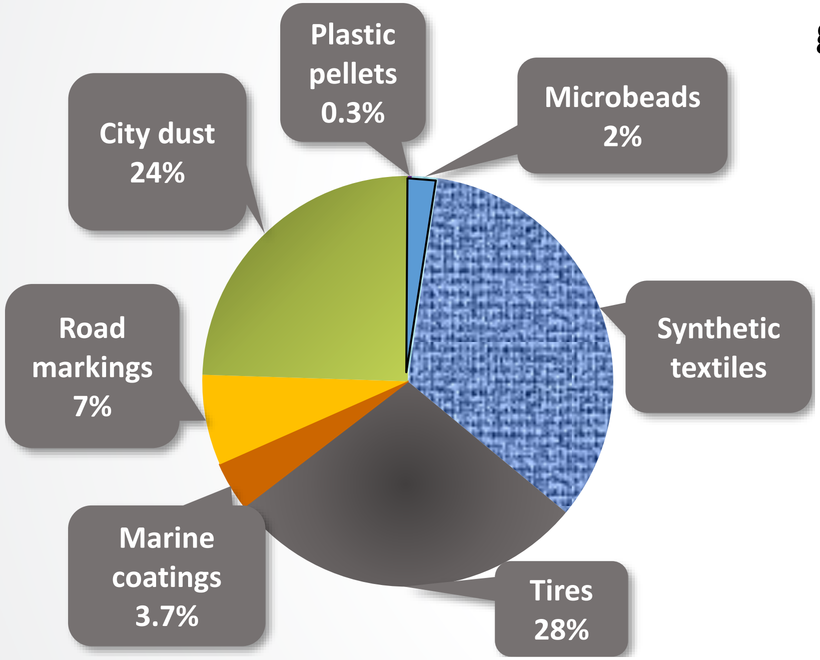
Primary plastic production

382 Mt produced in 2015, generating 302 Mt in environmental waste

Polymer	Code	Total plastics produced since 1950 (Mt)[a]	Mass % of total nonfiber or fiber since 1950[a]	Primary production in 2015 (Mt)	% of total produced in 2015	Applications
Nonfiber plastics[b]						
Polyethylene (PE): - low density (LD) - linear low density (LLD) - high density (HD)	LD, LLD: 4 HD: 2	2628	36	**64** (LD, LLD) **52** (HD)	**17** **14**	Plastic bags, storage containers
Polypropylene (PP)	5	1533	21	**68**	**18**	Rope, bottle caps, gear, strapping
Polyvinylchloride (PVC)	3	876	12	38	10	Pipe, film, containers (69% used in building & construction)
Polystyrene: expanded, extruded (EPS, XPS)	6	<730	<10	25	7	EPS: cooler boxes, cups, floats XPS: containers
PE terephthalate (PET, PETE)	1	<730	<10	33	9	Bottles, strapping
Polyurethane (PUR)	_	<730	<10	27	7	Durable foams (insulation, etc.)
Fiber plastics						
Polyester, polyamide (PA), & acrylic (PP&A)	-	1000	70% PES, 30% PA&A	**59**	**15**	Textiles, nets, ropes

[a]Estimates for 2015 (Geyer et al. 2017)

MP sources: direct release to oceans

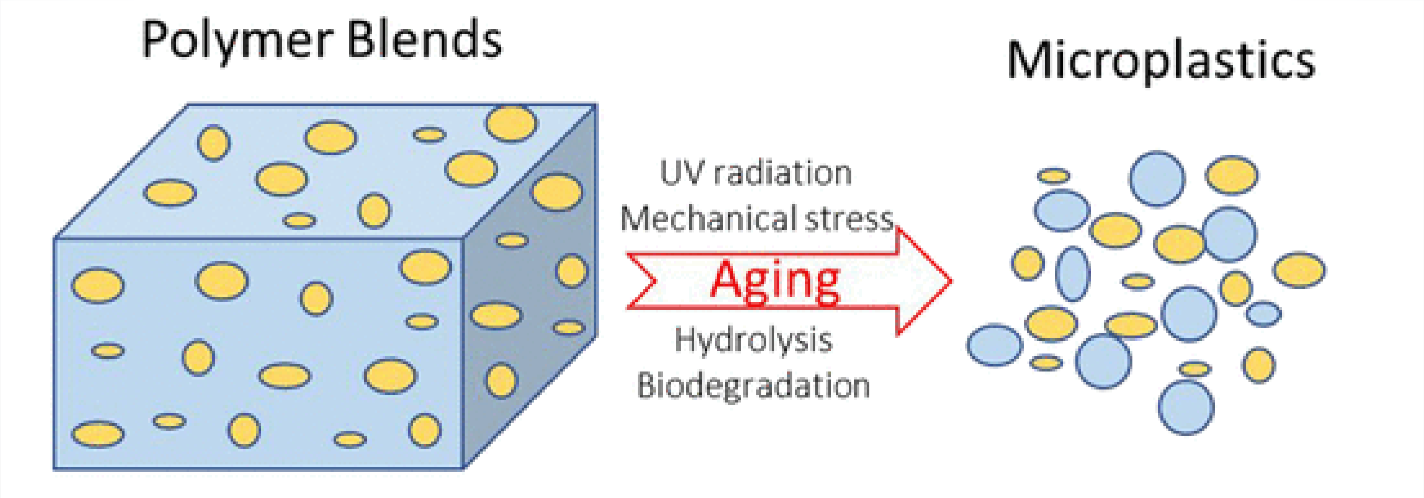


Source: International Union for Conservation of Nature and Natural Resources (IUCN) .

Microfibers from synthetic textiles may be a much greater problem than originally thought:

- Of the total plastics released to oceans (4.8 - 12.7 Mt/year), 15% - 31% could originate as MPs from homes and industrial products. About half of the total (3.2 Mt/year) MPs released, or about 1.5 Mt/year, ends up in oceans.
- Nearly two-thirds of the total MPs released is attributed to washing synthetic textiles (35%) and tire wear (28%). Microbeads represented just 2%.
- MP releases to oceans by Europe and Central Asia alone equivalent to 54 plastic bags per person year. Global average = 43 (North America = 150)

Emerging MP types: blends



Source: Wei et al. 2021

Emerging MP types: tires

REPORT

A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon

Zhenyu Tian[1,2], Haoqi Zhao[3], Katherine T. Peter[1,2], Melissa Gonzalez[1,2], Jill Wetzel[4], Christopher Wu[1,2], Ximi...
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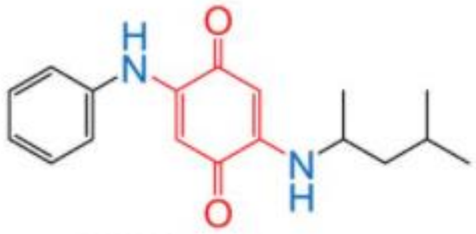
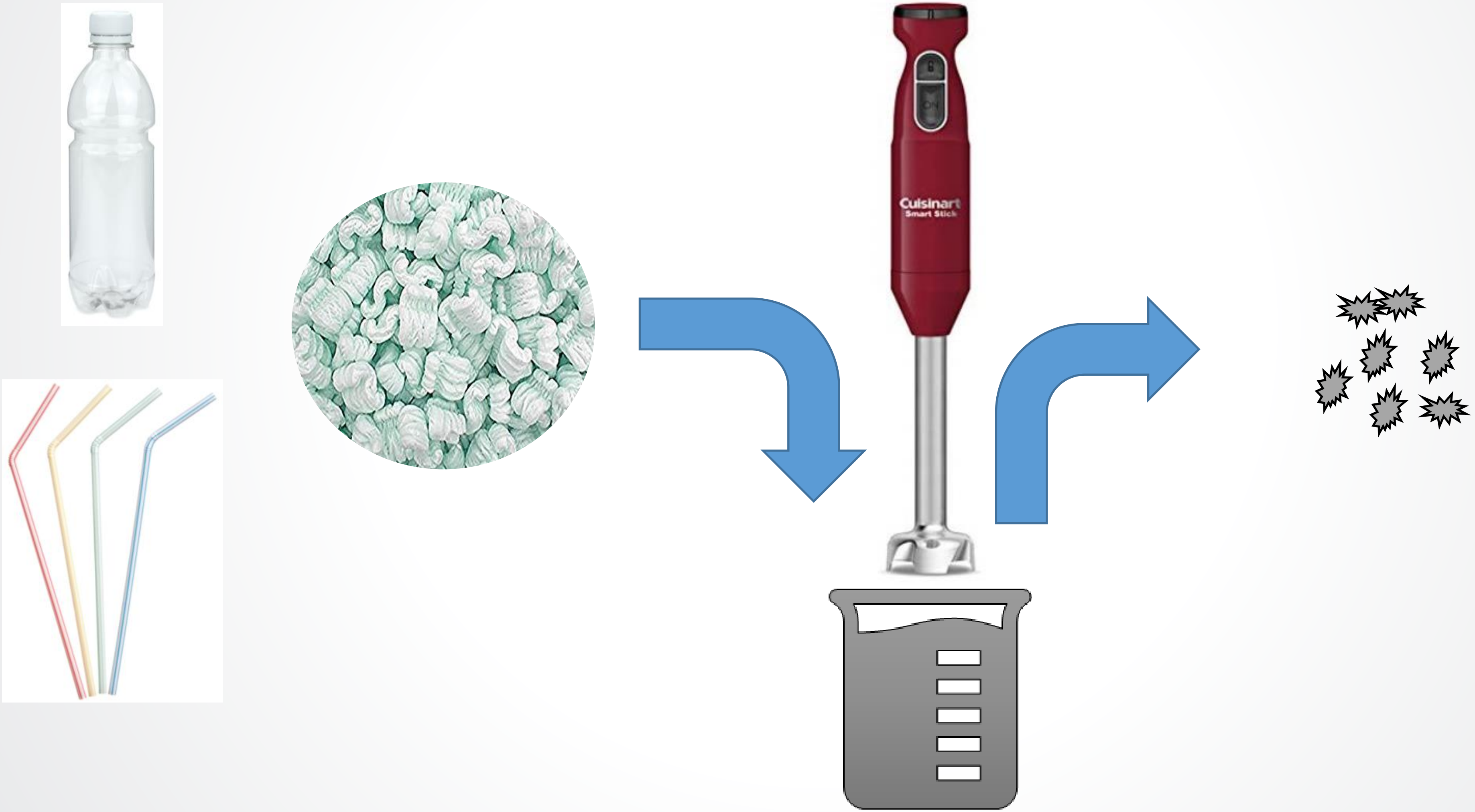


6PPD-quinone

Critical need: standards for exposure studies



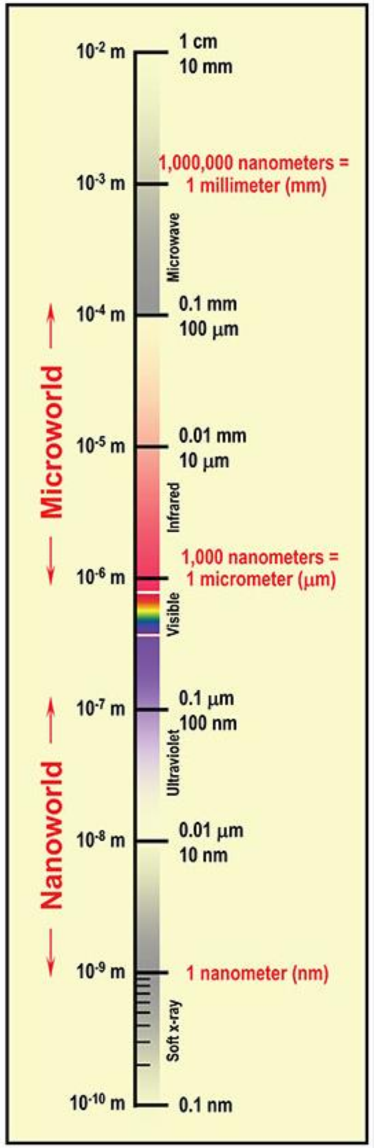
Nanoplastics

- Any regulation that is designed with regard only to microplastics release will likely be insufficient in affecting nanoplastics release
- We have the opportunity to include nanoplastics in our current investigations into microplastics rather than approaching them as two separate problems

NPI complications and risks

- Purification – bypass filtration methods intended for MPs
- Mobility – less likely to settle, transport further
- Uptake – more likely to enter food chain and bioaccumulate
- Toxicity – more surface area allows faster leaching of plastic additives
- Pollutant vector – more surface area for adsorption of metals and POPs

Critical need: nanoplastic definition



< 5 mm accepted definition of microplastics (MPs)

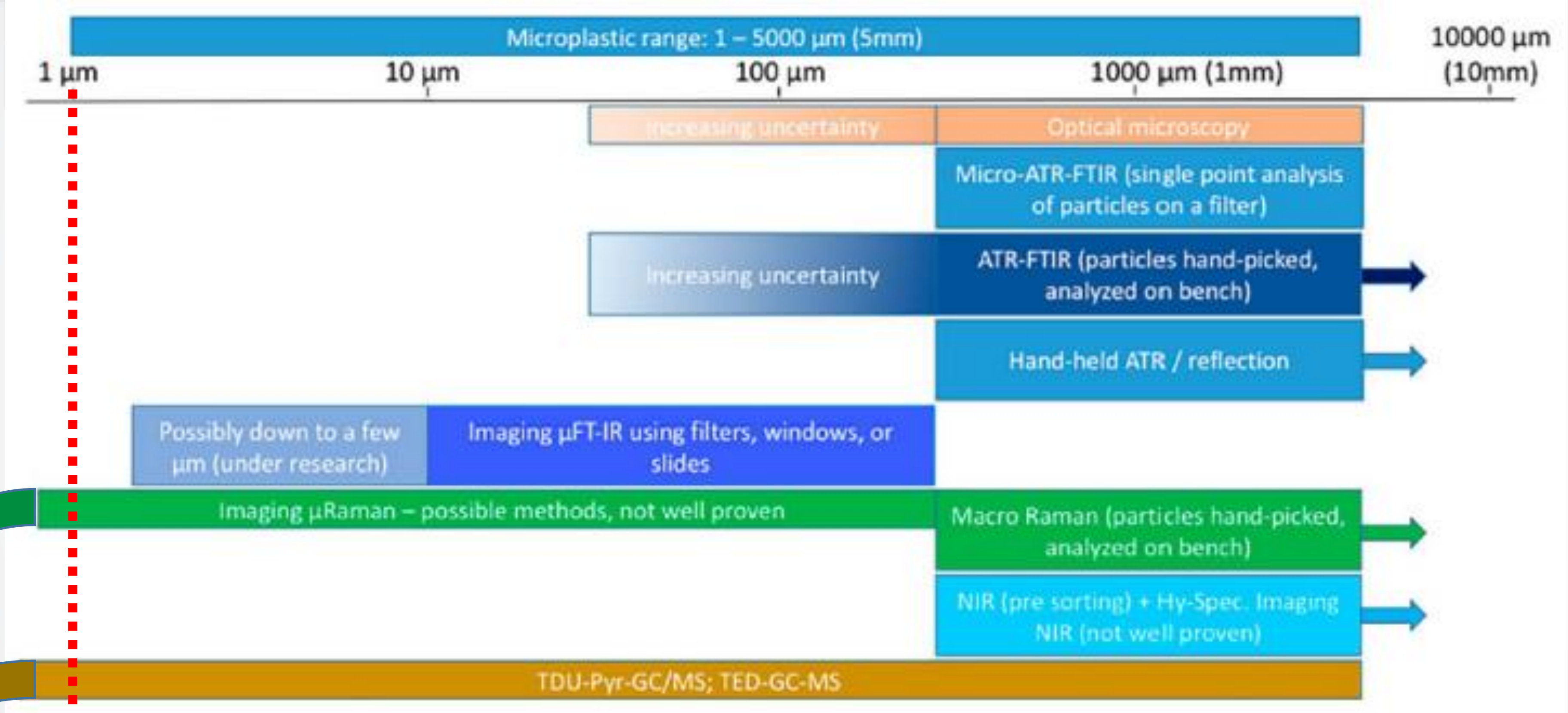
< 10 µm typical MP detection methods are less accurate or stop working

1 µm – 100 nm overlooked by standard nanoscale definition

100 nm – 1 nm nanoscale

Source: *Office of Basic Energy Sciences, U.S. DOE*

MP methods overlook NPls

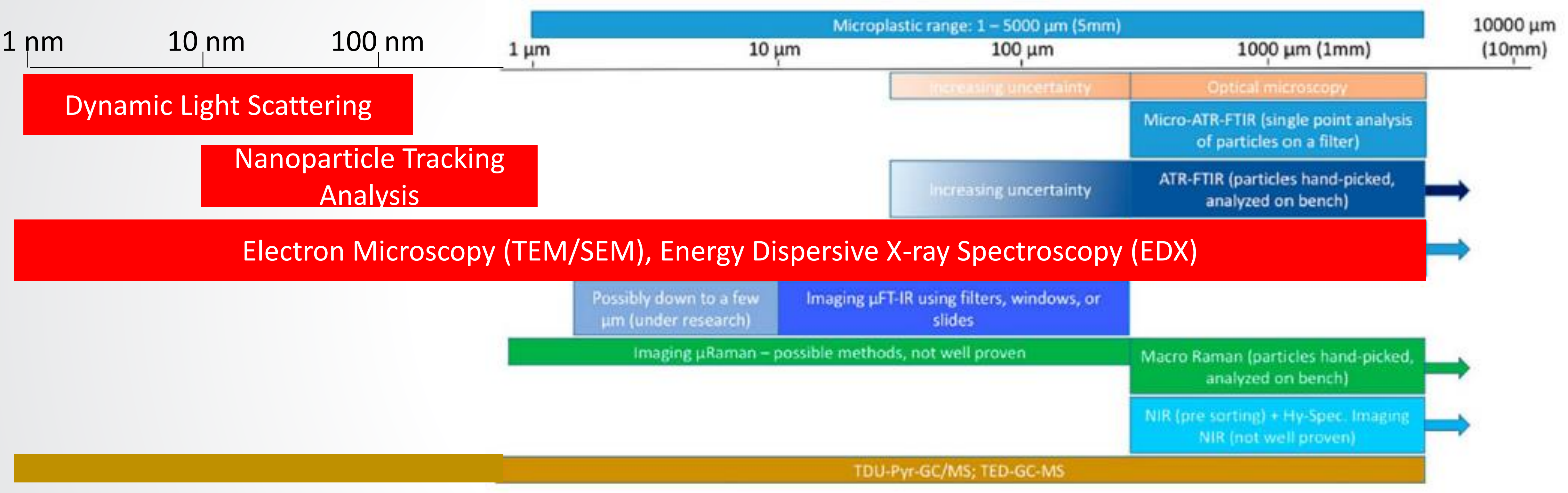


Recent advances, not well proven

No size restriction, but does not give particle size/shape

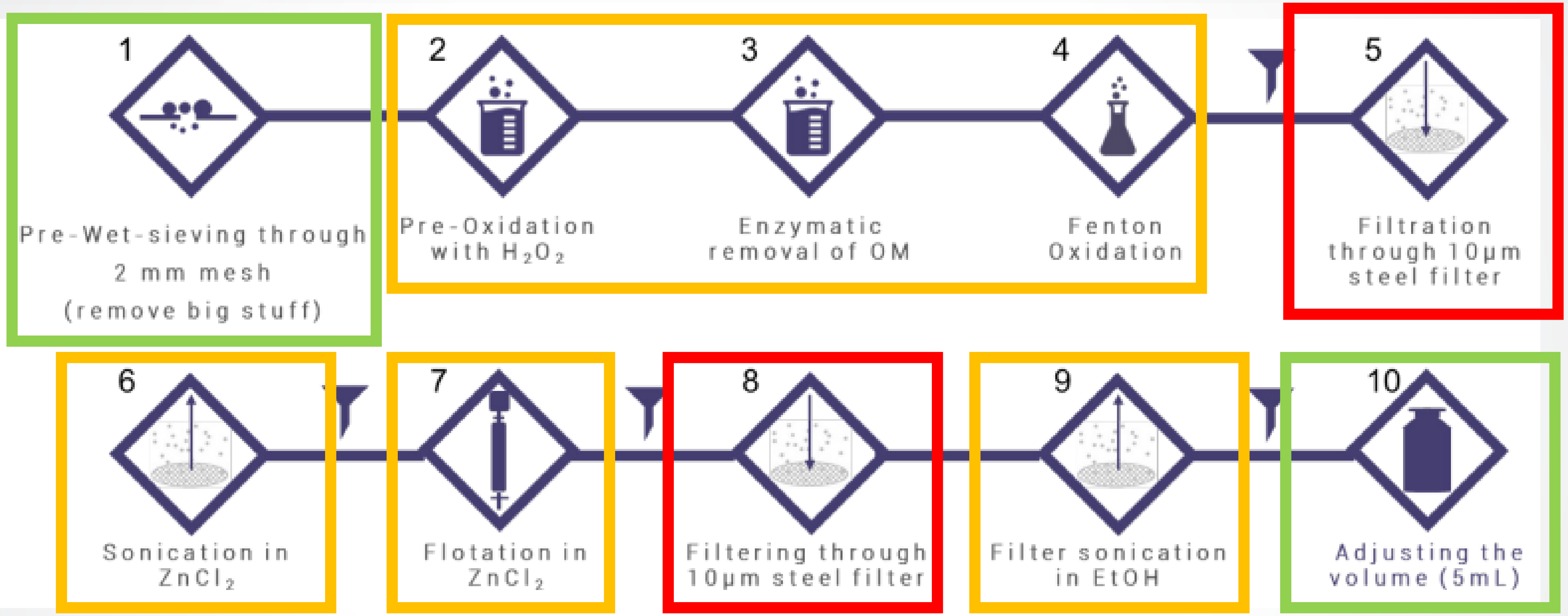
Source: *Agilent Technologies, Inc.*

Existing methods from nanotechnology



Distinguishing between NPls and other nanomaterials is the obstacle, better extraction methods needed to eliminate interferences!

MP extraction methods ignore NPls



- Other methods are used, including different flotation media, filter sizes, oxidation reagents

No loss of nanoplastics

Possible loss of nanoplastics

Definite loss of nanoplastics

Source: *Agilent Technologies, Inc.*

Current dilemma

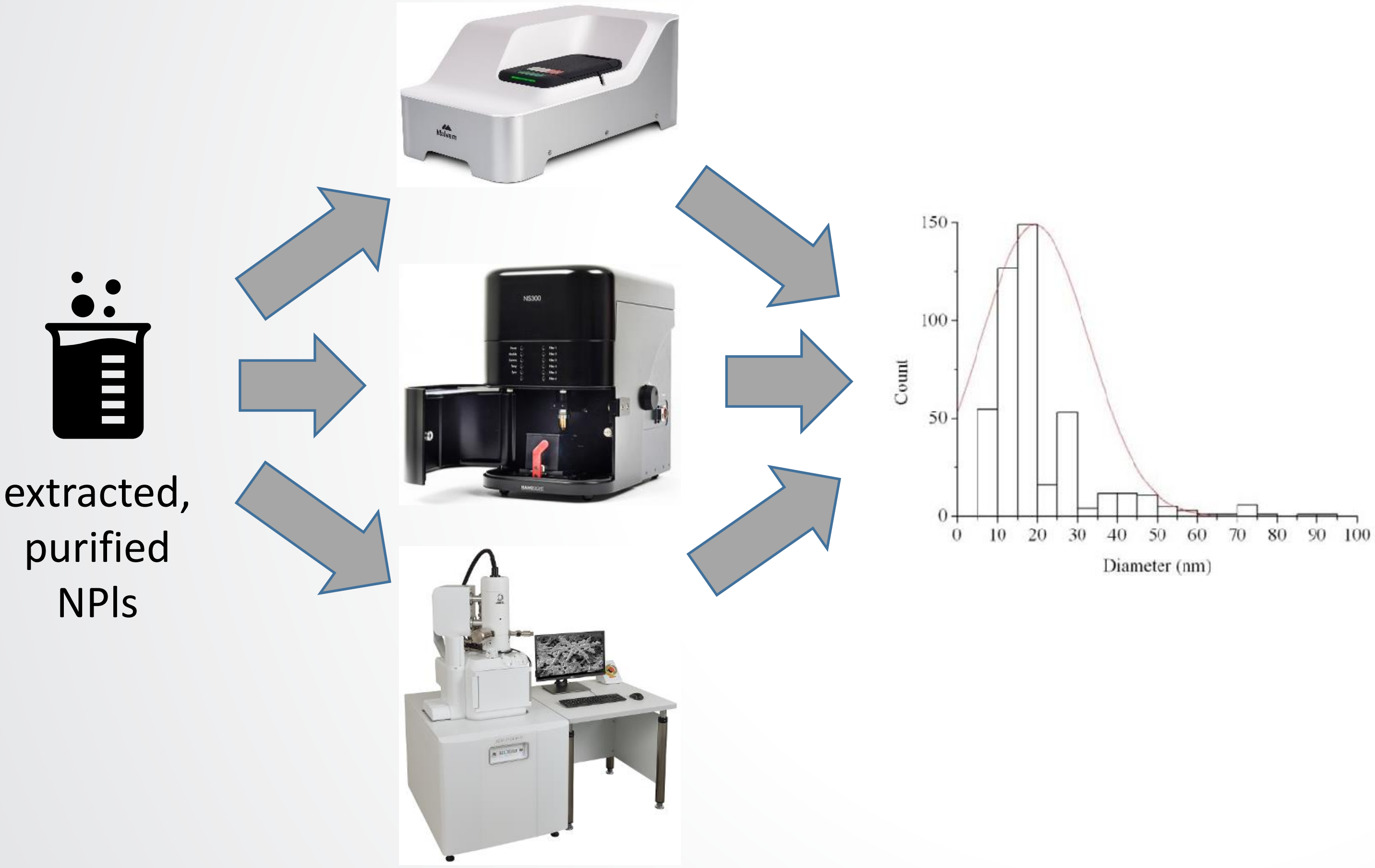
? • Can’t develop a detection method without an adequate extraction method to eliminate nanomaterial interferences

✓
- Use polymer nanosphere standard reference materials to:
  - confirm DLS, NTA, and TEM ability to detect NPls
  - test MP characterization techniques (micro-Raman/FTIR)

? • Can’t develop an adequate extraction method without a viable detection method to confirm extraction

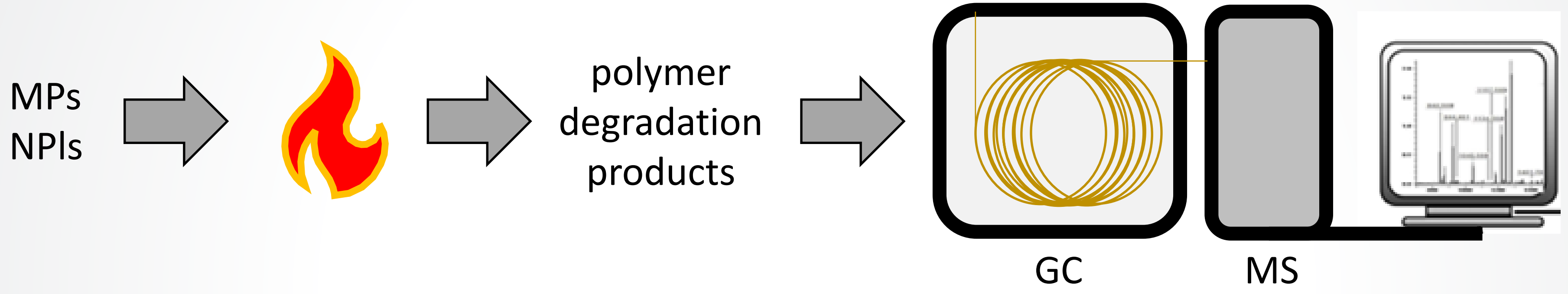
✓
- Use polymer nanosphere standard reference materials to:
  - test existing MP extraction methods for NPls
  - adapt extraction methods with new filters, flotation media, settling times

What can we learn from nanomaterials?



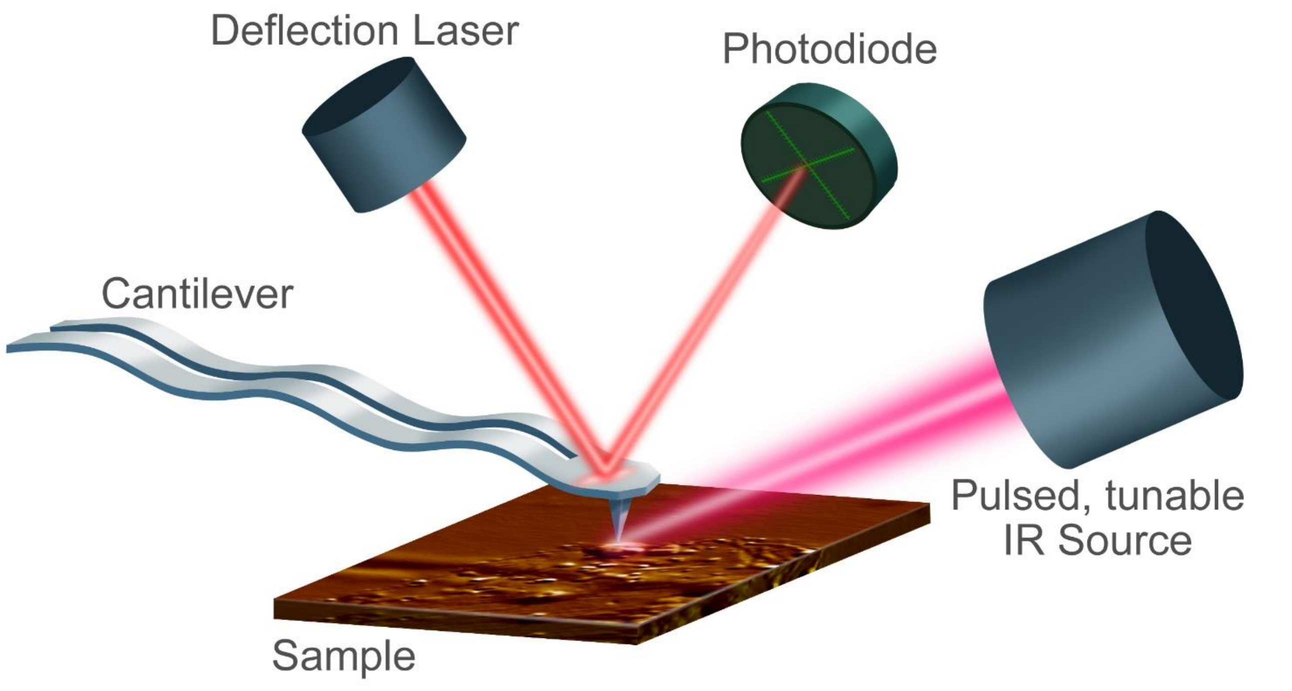
- Dynamic Light Scattering (DLS), Nanoparticle Tracking Analysis (NTA), and electron microscopy (TEM/SEM) all commonly used in nanomaterial characterization
- All give similar information – size/shape
- Not sensitive to composition – vulnerable to nanomaterial interferences

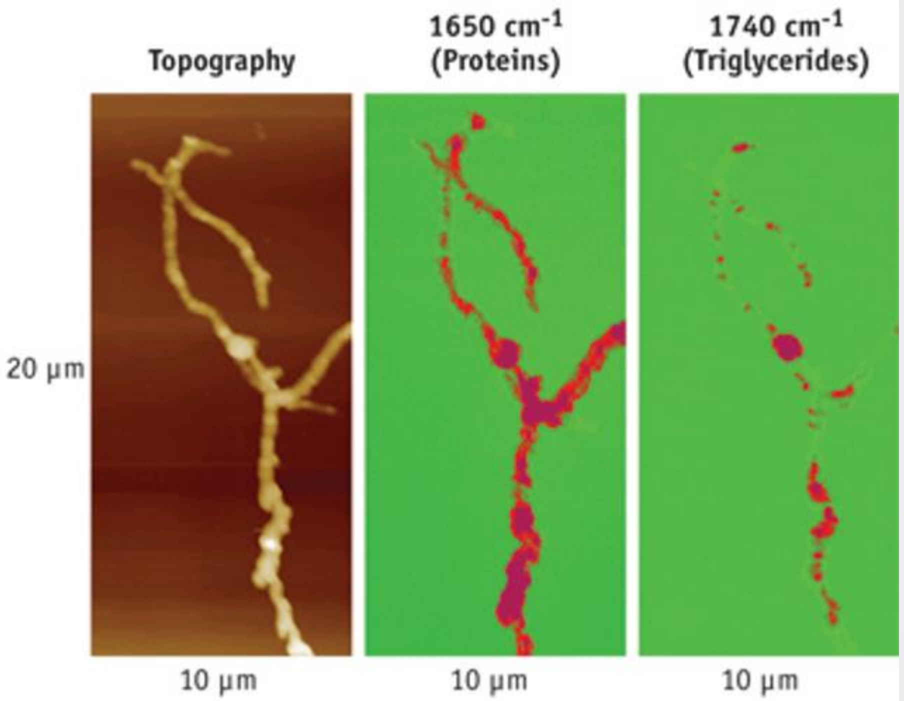
Emerging techniques – Pyr-GC/MS



- Thermal degradation products vary by polymer type but are not affected by particle size/shape
- Recent advances in sample preparation allow minimal pre-treatment in comparison with other techniques
- NPls included in results, but no differentiation between MPs and NPls

Emerging techniques – AFM-IR

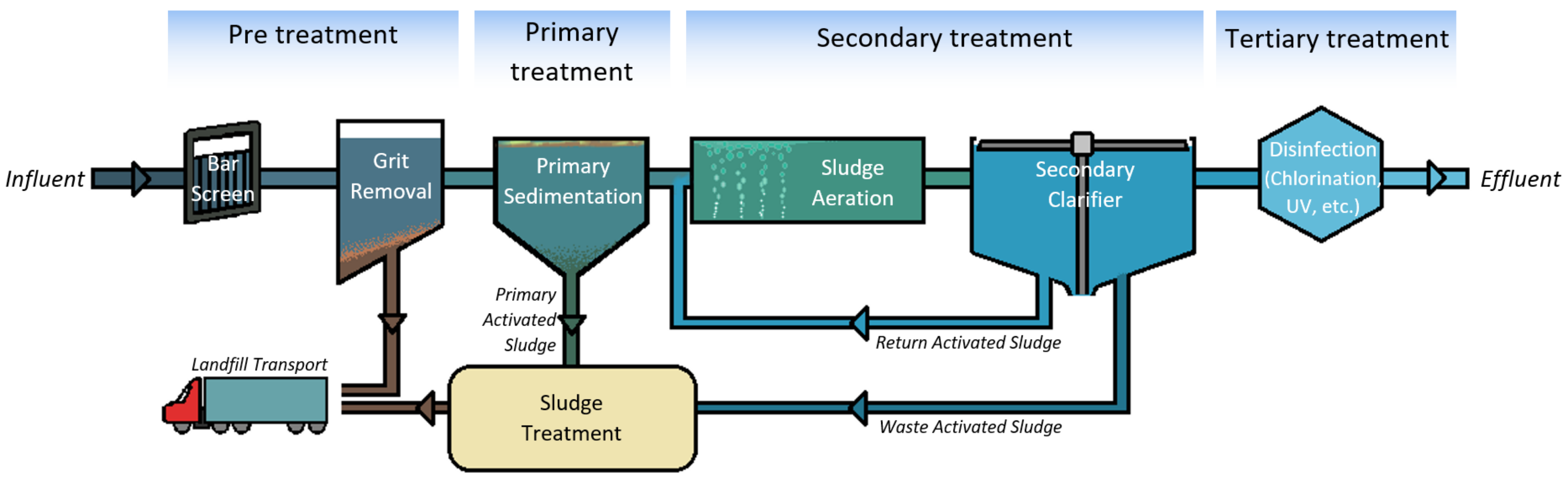




- Excitation by IR source causes oscillation of cantilever
- Currently capable of ~100 nm resolution
- Yields size/shape/polymer identification

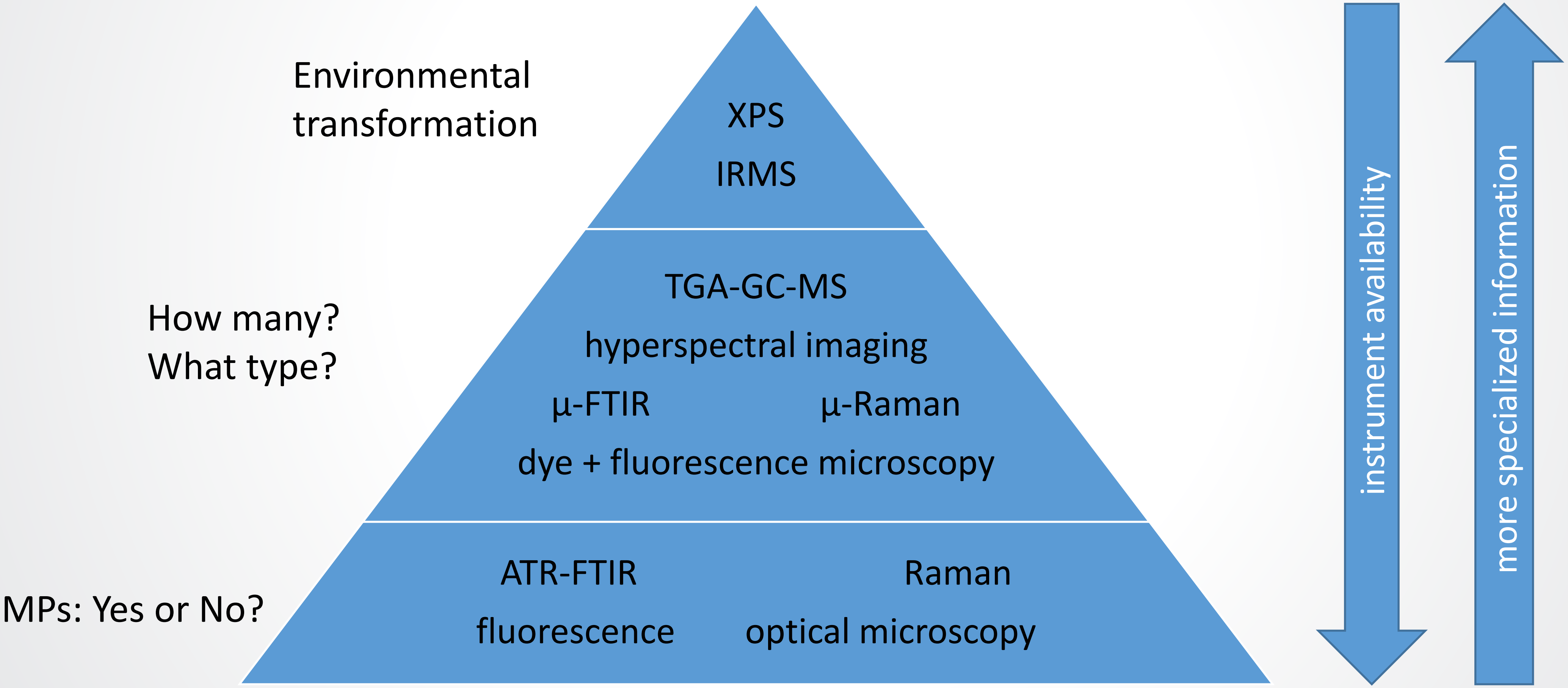
Source: *Anasys Instruments Corp.*

WWTPs remove microfibers and other MPs



- MP capture thought to relate to floatation and removal in grease by skimmers in primary treatment.
- Surface fouling/flocculation also may occur, causing MPs to sink in settling tank and/or associate with flocculants.
- MP removals of 96-99% are typical after secondary treatment. However, WWTPs release MPs due to high discharge volumes, and because they concentrate in sludge, which is used as fertilizer.

MP analytical techniques



Summary

- Need for standard size range for NPls: 1 – 1000 nm
- Even in studies that focus on MPs, NPl standards should be included in evaluating extraction/detection efficiency
- Nanoplastics possibly pose a greater risk than MPs due to increased number, mobility, and reactivity; there is a critical need for:
  - New methods for extraction of nanoplastics from environmental media
  - Investigating nanoplastic properties (formation, adsorption, aggregation)

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